

Note on the Specific Heat of Water.

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In a paper on the "Specific Heat of Water and the Mechanical Equivalent of the Calorie"** were given the figures from 0° to 80° C. which resulted from our investigation. These figures agreed very fairly with those of some other observers,† but differed considerably from the corrected figures of Callendar and Barnes.‡ In our curve there was a minimum value of the specific heat at about 25° C., and a rapid rise afterwards from 25° to 60° of nearly the same magnitude as the fall from 0° to 25° . In the curve of Callendar and Barnes the minimum was not reached till 38° C., and thereafter the rise was much slower.

Callendar soon after devised a novel method of "continuous mixture" by means of an ingeniously devised heat exchanger, and applied this apparatus to test his former results in this range between 60° and 100° . Water at about 100° C. from a heater was passed through the heat exchanger against water from a cooler at from 25° to 35° C. The result of these experiments indicated that the ratio of the mean specific heat from 69° to 100° C. to the mean specific heat from 25° to 56° C. agreed within 1 in 5000 with the ratio derived from Callendar's formula based on the figures of Callendar and Barnes. These results of this new method were published in Callendar's Bakerian Lecture in 1912,§ and were made the basis of a criticism of our results and those of other observers.

The value of our results in the range which compares with Callendar's new method depends entirely upon the reliability of the correction for evaporation within this range, which is shown graphically in fig. 8 of our paper. A glance at that figure shows that it is not till the temperature of 55° is passed that our correction for evaporation becomes unreliable. We pointed out, with reference to this correction, that :—

"Between 70° and 80° there appears to be considerable uncertainty, especially from 75° to 80° C. This may be partly owing to differences in the amount of air contained in the water, which tends to come off at about this temperature ; but it is probably due to some variability in the amount of escape of moisture through the holes in the obturator as the vapour pressure rises."

* W. R. Bousfield and W. Eric Bousfield, 'Phil. Trans.,' A, vol. 211, p. 199 (1911).

† See figs. 10 and 11, *loc. cit.*, p. 237.

‡ See Barnes, 'Roy. Soc. Proc.,' A, vol. 82, p. 390 (1909).

§ 'Phil. Trans.,' A, vol. 212, p. 1 (1912).

We have therefore no hesitation in accepting the superior accuracy of the results of Callendar's new method in this region. But Callendar's new figures have only a remote bearing on the values in the lower range and the true position of the minimum. To test the values in the range from 0° to 55° the new method has not been applied, and the difficulties which it was specially designed to meet at higher temperatures hardly exist in the lower range. Over this range the vapour pressure of water is so small that an accurate correction for evaporation can be easily made. The figures which we obtained were closely in line with those of other observers, and the question whether they are more or less correct in this range than those of Callendar and Barnes still appears to be an open one.

According to our corrected figures, the mean specific heat from 13° to 26° is almost exactly equal to that from 26° to 39° , which gives the minimum value in the neighbourhood of 25° . It should not be difficult to apply Callendar's new method to determine this ratio. In the meantime, it is desirable to point out what are the outstanding differences in this lower range, and to refer to some new experiments confirmatory of our former figures. The salient differences in this range of temperature are as follows:—

1. The fundamental figure which was determined by our experiments was the total heat of distilled water, air freed, and having a conductivity of only 1×10^{-6} , between 13° and 55° . The value obtained for the mean specific heat of water from 13° to 55° was

$$4.182 \text{ joules.}$$

The corresponding figure which results from Callendar and Barnes' observations is

$$4.177 \text{ joules.}$$

2. The minimum value for the specific heat of water according to our experiments is at 25° , and according to those of Callendar and Barnes at 38° .

3. The specific heat of water at 20° C. deduced from our experiments was

$$4.176 \text{ joules.}$$

That deduced from the experiments of Callendar and Barnes was

$$4.180 \text{ joules.}$$

As to the first point of difference the following observations may be made : The experiments on which our figure was obtained were fairly large scale experiments, there being 3 litres of water in the calorimeter. They were continuous-flow experiments, into which entered no consideration of the capacity of the calorimeter. They were the result of three sets of experiments, each set of experiments having an ascending order of agreement

between individual experiments. Before the last set of experiments the electrical standards and the standard thermometers had all been recently and very carefully re-calibrated at the National Physical Laboratory.

The individual results of the last set of experiments were:—

No. of experiment.	Inflow.	Outflow.	Value of $J_{13}^{54.25}$.
161	13.003	53.932	4.1783
162	12.978	54.88	4.1779
164	12.98	54.14	4.1785
165	12.973	54.16	4.1795
166	12.99	54.137	4.1785
Mean			4.1785

The mean of these was the value 4.1785 for tap water. The maximum difference between individual values and the mean was less than 1 in 4000.

The range of temperature being 13° to 54°, it was estimated that there might be an error of 0.01 in the temperature readings of any of these 40° intervals. The result shows that the mean error was less. There was no chance of any zero error creeping into the results.

These experiments, each of which involved the use of a large quantity of water, were made on "tap water." The resulting figure was used to determine the capacity of the calorimeter. A series of fifteen subsequent experiments on air-free distilled water over the same range showed that its mean specific heat was slightly higher, viz., 4.182 from 13° to 55°. Subsequently the total heat of water for each of the three intervals, 13°–27°, 27°–40°, 40°–55°, was determined by four series of experiments, and the sum of the total heats so determined was precisely the same as that directly determined, again giving 4.182 for the mean specific heat from 13° to 55°.

It is suggested that there may be some hidden systematic error in the method. This is, of course, possible, but it seems to be equally possible in the continuous-flow method with platinum thermometry on which the figures of Callendar and Barnes were founded. As a practical unit for calorimetric work the mean specific heat from 13° to 55° still stands pre-eminent, since it can be readily reproduced at all seasons of the year, and easily applied to ascertain accurately the capacity of any calorimeter, a figure which is necessary for nearly all calorimetric work on solutions, where the quantity of solution required forbids the continuous-flow method in most cases.

As to the second point of difference, the position of the minimum, the

following observations may be made: The course of our curve from 0° to 40° with its minimum at about 25° is in general agreement with the curves of Lüdin, Rowland and Bartoli and Stracciati, whilst the course of the Callendar and Barnes' curve with its minimum at about 38° differs from all.

The results of a paper on the specific heat of certain solutions presented simultaneously with this note confirm our position of the minimum very substantially.* The old Dewar vessel having been broken it was required to determine the mean capacity of a new and heavier vessel over the intervals 0° - 13° , 13° - 26° , 26° - 39° . A completely different method of regulating the electric current was adopted. In the former experiments the current was kept constant by the use of an ampère balance and simultaneously of a battery of standard cells. In the present experiments the current was regulated so as to keep the energy supply constant by means of a Kelvin watt balance. Moreover, the system of corrections for small heat gains or losses was entirely changed. The capacity was determined by a series of twelve experiments which are set out in the simultaneous communication.

For any interval a° to b° , the total heating of the calorimeter and its contents is given by

$$WS_a^b + C_a^b = 60U \left| \frac{d\theta}{dt} + \frac{dQ}{d\theta} \right|$$

where W is the weight of water, S_a^b the mean specific heat of water for the interval, C_a^b the mean capacity of the calorimeter for the interval, U the electrical watts, $d\theta/dt$ the mean rate of rise of temperature per minute and $dQ/d\theta$ the correction for small heat gains or losses. From these experiments the mean values for the quantity on the right-hand side were determined as

	0° - 13°	13° - 26°	26° - 39°
Joules	13421	13382	13401.

The mean value of W was 3000·1 grm.

The mean values of S_a^b derived from the former paper, after making a minute correction for the slight variation of capacity of the calorimeter which arises from the expansion of the water from 0° to 39° were

	0° - 13°	13° - 26°	26° - 39°
S_a^b =	4·193	4·175	4·175

whilst the corresponding values of S_a^b from Callendar and Barnes' figures are

$$S_a^b = 4·199 \quad 4·189 \quad 4·184.$$

* This paper will appear in the 'Philosophical Transactions.'

The respective capacities derived from the first set of figures are

$$C_a^b = \begin{array}{ccc} 839 & 857 & 876 \end{array}$$

whilst those derived from the second set of figures are

$$C_a^b = \begin{array}{ccc} 824 & 815 & 849. \end{array}$$

As the specific heat of glass steadily increases with rise of temperature it is obvious that the second set of capacities is inadmissible. The irregularity of the second set clearly arises from the shifting of the minimum which these figures involve and the regularity of the series of capacities derived from our figures supports the view that the minimum is in the neighbourhood of 25° , which gives almost equal values for S_{13}^{26} and S_{26}^{39} and not diminishing values.

A further confirmation results from a consideration of the actual values of the specific heats of the KCl and NaCl solutions.

The phenomenon of the minimum value of the specific heat of water undoubtedly arises from the fact that the large proportion of ice-molecules contained in water at the lower temperatures is considerably reduced with rise of temperature, whilst a little later the increasing proportion of steam molecules tends again to increase the specific heat. In saturated solutions of KCl and NaCl the proportion of ice and steam molecules is greatly reduced, and the solvent becomes mainly simple dihydrol. The figures for these solutions indicate a nearly straight line law from 0° to 39° between specific heat and temperature. The fact that the temperature-specific heat curves for saturated solutions of KCl and NaCl come out as nearly straight lines can hardly be a mere coincidence and it entirely depends on getting the right relative values for the capacities for the three intervals.

Until the course of the specific heat curve from 0° to 40° can be considered as definitely settled there must remain a doubt as to the value of the 20° calorie amounting to 1 part per 1,000. The reasons for adopting as the standard calorie the mean specific heat over an interval which undoubtedly includes the minimum point upon either view and which is easily reproducible were stated in the former communication.* The interval from 13° to 55° satisfies all the practical conditions and there remains a difference of over 1 part per 1000 between our value for the interval and that which results from Callendar's latest figures. It may be hoped that Prof. Callendar may be able to apply his new method to a direct test of the values over this range.

* *Loc. cit.*, p. 42.